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Adsorption and dissociation of hydrogen on MgO surface: A first-principles study

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ABSTRACT

Periodic density functional theory (DFT) has been used to investigate the adsorption and dissociation of hydrogen on MgO surface. Weak molecular adsorptions were observed and the bridge site with the vertical mode was the most favorable molecular adsorption site. The reaction barrier along with dissociation of the hydrogen molecule on the MgO(0 0 1) surface has also been studied. Our results show the most favorable dissociation channel needs activation energy of around 2.2 eV at the bridge site which is in agreement with the previous results (2.34–2.94 eV). The minimum energy pathway for surface diffusion of atomic H indicates the existence of small classical barriers with a value of about 0.37 eV. And our calculations show that H atom can diffuse from the surface sites to subsurface and further into the bulk sites. The most stable absorption configurations are the interstitial octahedral sites in diffusion movements. The largest barrier in these processes is up to 1.52 eV in the diffusion step of surface to subsurface. Once atomic H penetrates the subsurface layers, the corresponding diffusion barriers decrease to 1.02 eV (from subsurface-1 (SB1) to subsurface-2 (SB2) site) and 1.2 eV (from SB2 to subsurface-3 (SB3) site), respectively.

Our calculations indicate that dissociation of molecular hydrogen is strongly inhibited on the magnesium oxide surface during the hydrogenation on magnesium films.

1. Introduction

Hydrogen is an ideal clean carrier for storage, transport, and conversion of energy. However, a key problem is its storage, especially for its use as a fuel for zero-emission mobile applications. Nowadays, there is considerable research on magnesium and its alloys for hydrogen storage due to their high hydrogen storage capacities by weight and low cost. One of the main disadvantages of Mg-based hydrogen storage alloys is the ease of making a closed oxide layer on its surface which impedes hydrogen absorption [1]. The phenomena are underlined by the observation that the adsorption kinetics of any metal hydride system strongly depends on sample pretreatment and residual gaseous contaminations such as O_2, H_2O or CO [2]. Metals with clean surfaces react generally very fast with hydrogen, as nearly all metals have a strongly negative chemisorption enthalpy for hydrogen. However, nearly all metals forming hydrides are usually covered with a stable oxide skin when they are exposed in air, water or other oxygen atmospheres due to the large negative heat of oxide formation [3]. Andreasen et al. [4] reviewed the kinetics in terms of the kinetic triplet (E, the activation energy; A, the pre-exponential factor and $f(\xi)$, the reacted fraction) of reaction between Mg-based alloys and hydrogen and found that variations in the apparent activation energies correlated with the presence of an MgO surface layer inhibiting diffusion of hydrogen. Friedrichs et al. [5] reported that a universal oxide passivation layer of about 3–4 nm in thickness prevented the samples from further oxidation.

Theoretical studies on the surface properties of MgO and hydrogen adsorbed on the MgO thin films have been extensively investigated [6,7]. *Ab initio* calculations have been performed for H_2 interacting with a temperature-reconstructed MgO(1 1 1) surface, created from a molecular dynamics simulation at 300 K [8]. Results show that the physi- and chemisorption properties for the H_2/MgO(1 1 1) system are very sensitive to the surface structure. And the adsorption energy of the most attractive surface site for H_2 chemisorption on the ideal (1 1 1) surface is −480 kJ/mol, while for that of the reconstructed surface is about −60 kJ/mol. Kobayashi et al. [9,10] used *ab initio* MO method to investigate the dissociative adsorption of the hydrogen molecule(s) on the MgO(1 0 0) surface and found that an activation energy of 2.94 eV (restricted Hartree–Fock, RHF) or 2.34 eV (second-order MΦller–Plesset perturbation, MP2) was required to overcome the barrier of dissociation. Gonzalez et al. [11] applied the infrared absorption of OD^- and OH^- ions to study diffusion rates of D^+ and H^+ in doped and undoped MgO crystals. Experiment results showed that no activation barrier could be

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obtained for pure MgO because no diffusion could be measured below the maximum operating temperature of the equipment, 1750 K. However, MgO:Li is an anomaly among MgO crystals in the lowest temperature of 800 K with an activation energy of 1.9 ± 0.2 eV.

From mentioned above, it is not difficulty to find that few theoretical studies are related to hydrogen storage and especially little is known about the adsorption geometries, dissociation on MgO surfaces and diffusion pathways of H both on MgO surfaces and in the bulk. It is well known that dissociative or molecular path is one of important approaches for increasing hydrogen stored amount per unit weight in Mg-based materials. In order to illustrates this question, a better knowledge of the structures and stresses including in the physical adsorption and chemical adsorption and diffusion processes is in turn required [12].

In this paper, we presented results for the properties of H_2 molecule and bulk MgO. Then we considered the process of adsorption of hydrogen on MgO surface. Further, the process of dissociative chemisorption of H_2 on MgO(0 0 1) surface has been investigated. Finally, we analyzed the minimum energy pathway (MEP) for diffusion of H between different surface sites and for diffusion from surface to subsurface sites.

2. Computational methods and models

The calculations were done using the Vienna *ab initio* simulation package (VASP) [13]. This program evaluates the total energy of periodically repeating geometries based on density functional theory and the pseudopotential approximation. In this case, Kresse and Joubert [14] successfully applied the projector augmented wave (PAW) method proposed by Blöchl to describe the electron–ion interaction. The pseudopotentials are the Troullier–Martins type [15]; the core radii are 0.700 Å for H ($1s^1$ core), 1.550 Å for O ($2s^2$ $2p^4$ core) and 2.880 Å for Mg ($2p^6$ $3s^2$ core). The local density approximation (LDA [16]) was used for the exchange–correlation potential. All energies were calculated at $T = 0$ K. The minimization of the electronic free energy was obtained using an efficient iterative matrix diagonalization routine based on a sequential band-by-band residuum minimization method (RMM) [17]. The optimization of different atomic configurations is based upon a conjugate gradient minimization of the total energy. The value of the energy cutoffs and the k-point grids were chosen to ensure the convergence of energies and structures.

We used a periodic six-layer structure with thickness of 10.32 Å to calculate a clean surface and the adatoms adsorbed on one side of the slab. A (2 × 2) surface unit cell was used for calculations because of its stable with low cleavage energies relative to the other surfaces [18]. The corresponding kinetic energy cutoffs were 400 eV for PAW calculations. Brillouin-zone integration was employed with a 5 × 5 × 1 Monkhorst–Pack [19] grid of k-points for all the supercells. The slab was separated from its periodic image in the direction normal to the surface by a vacuum space of more than 18 Å. Three surface layers were allowed to relax and bottom layers were fixed in their optimized bulk positions.

An improved version of the nudged elastic band (NEB) method, the climbing-image NEB [20], was used to locate the minimum energy pathways and the transition states (TS) for the diffusion of hydrogen adsorption on MgO surface. In calculations, all the images were relaxed until the maximum force acting on an atom was less than 0.01 eV/Å. A smaller set of k-points (5 × 5 × 1) and a lower energy cutoff (300 eV) were used for NEB calculations due to their computational expense. When the energy difference between the initial state and transition state on the clean surface was recomputed using more k-points (7 × 7 × 1) and a higher cutoff energy (400 eV), the activation barrier only differed from our original NEB result by 0.04 eV.

Table 1
Calculated equilibrium lattice constant (a_0), equilibrium volume (V_0) and bulk modulus (B_0) for bulk MgO using PW91 functional and USPP and PAW potentials, respectively.

Reference	a_0 (Å)	V_0 (Å^3)	B_0 (GPa)
This work LDA + PAW	4.23	75.69	171.1
LDA + USPP [32]	4.22	75.2	159
GGA + PAW [33]	4.25	77	150.6
Experiment [34]	4.21	74.7	160.2

3. Result and discussion

3.1. Calculations of H_2 molecule and bulk MgO

The accuracy of the computational method used in this study has been tested initially to describe the properties of H_2 molecule in gas phase. In this case, an isolated H_2 molecule has been optimized in a cubic box with 10 Å side. The bond length and bond energy of molecular hydrogen calculated from our DFT approach are $r_{\text{H–H}} = 0.749$ Å and $E_{\text{binding}} = 4.55$ eV without the zero point energy correction, in good agreement with the experimental values of 0.74 Å [21] and 4.52 eV [22], respectively, as well as to other similar GGA results [23].

Then the test was to predict the equilibrium properties of bulk MgO. In Table 1, we provide the results for the equilibrium lattice constant, equilibrium volume and bulk modulus of MgO together with corresponding experimental data and other previous calculations.

The results obtained in these tests made us confident in pursuing the next step of our investigations, namely the interaction of H atoms and molecules with MgO surface.

3.2. Adsorption of hydrogen on MgO(0 0 1) surface

The H_2 molecule was allowed to approach the MgO(0 0 1) surface along four different symmetrical sites: (i) directly on-top of a magnesium atom (on-top(Mg) site); (ii) directly on-top of an oxygen atom (on-top(O) site); (iii) at the middle of two nearest neighbor magnesium and oxygen atoms (bridge site); (iv) at the center of the smallest unit structures of the surfaces (center site). As the smallest structure of an MgO(0 0 1) surface is a square, these four sites are the only symmetrically distinguishable sites. The possible adsorption sites we examined for atomic and molecular hydrogen on clean MgO(0 0 1) are shown in Fig. 1. For each of these positions, we consider two approaches for adsorption paths. They are: (a) a H_2 molecule approaching vertical to the surface (vertical approach); (b) a H_2 molecule approaching parallel to the surface and parallel to the square lattice vectors (horizontal approach).

The adsorption energies for molecular and atomic hydrogen were defined as

$$E_{\text{ads-H}_2/\text{MgO}(001)} = (E_{\text{MgO}(001)} + E_{\text{H}_2}) - E_{\text{H}_2/\text{MgO}(001)} \quad (1)$$

and

$$E_{\text{ads-H/MgO}(001)} = \left(E_{\text{MgO}(001)} + \frac{1}{2}E_{\text{H}_2}\right) - E_{\text{H/MgO}(001)} \quad (2)$$

where $E_{\text{ads-H}_2/\text{MgO}(001)}$ and $E_{\text{ads-H/MgO}(001)}$ are the adsorption energy of systems with adsorbed H_2 molecule and H atom, respectively; E_{H_2} is the total energy of a H_2 molecule in the gas phase; $E_{\text{MgO}(001)}$ is the total energy of the MgO slab without adsorbed species; and $E_{\text{H}_2/\text{MgO}(001)}$ and $E_{\text{H/MgO}(001)}$ are the total energies of systems with adsorbed H_2 molecule and H atom, respectively. With this definition, positive values of adsorption energy denote that adsorption is more stable than the corresponding clean surface and gas phase H_2. The calculated adsorption energies do not include zero point energy corrections.

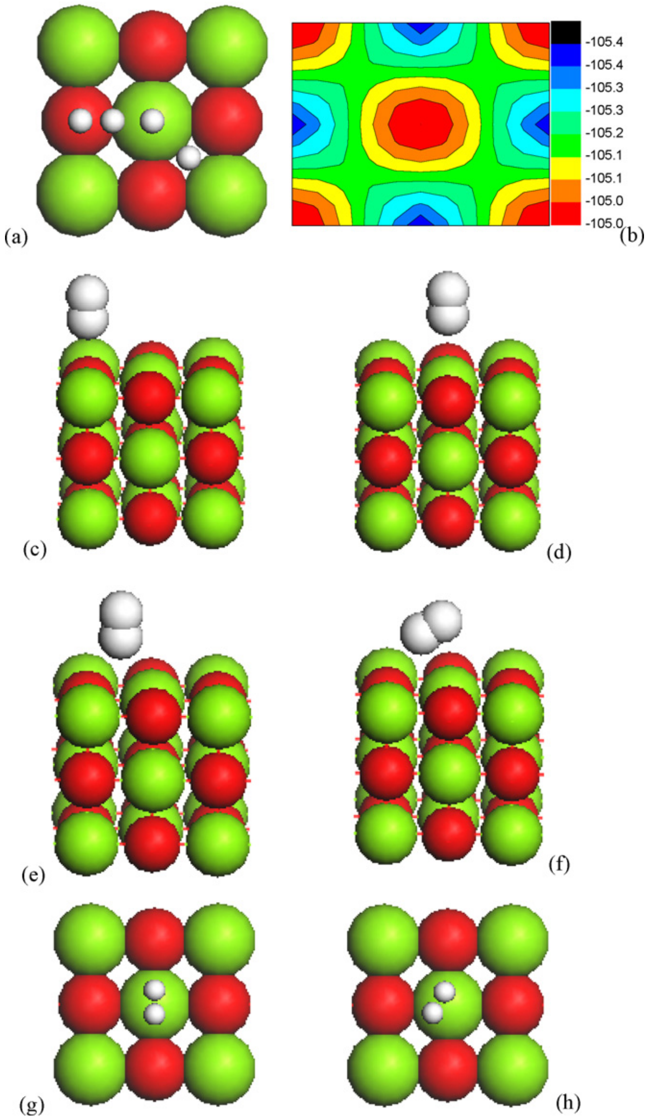

Fig. 1. Schematic representation of adsorption sites of H atom on MgO(0 0 1) surface: on-top(O) (left one), bridge (left two), on-top(Mg) (right two) and center (right one). (b) A 3D plot of the binding energy surface of a H atom in different positions over MgO substrate. For a given position (*X*, *Y*) over the MgO cell the distance *Z* of the H atom from the MgO plane was optimized in order to obtain the highest binding energy. (c)–(f) The on-top(O), on-top(Mg), center and bridge site for vertical approaches, respectively. (g and h) The on-top(Mg) and bridge site for horizontal approaches, respectively.

Table 2
Adsorption energies of H_2 adsorption on MgO(0 0 1) surface. Chemisorption parameters, r_d and r_H are the distances of hydrogen atom from the MgO(0 0 1) surface and the H–H distance, respectively.

Site	Approach	r_d (Å)	r_H (Å)	Adsorption energy (eV)
On-top(O)	Vertical	2.155	0.779	0.015323
	Horizontal	–	–	–[a]
On-top(Mg)	Vertical	2.399	0.769	−0.05383
	Horizontal	2.195	0.778	0.051853
Bridge	Vertical	2.078	0.779 (32.3°)	0.052836
	Horizontal	2.295	0.775	0.042186
Center	Vertical	2.268	0.772	−0.015182
	Horizontal	–	–	–[b]

[a] Move to adjacent magnesium.

[b] Move to bridge (vertical approach).

The adsorption energies, and the corresponding distances are given in Table 2. The distances r_d listed in the tables are the distances from the MgO(0 0 1) surface to the hydrogen atoms if both the hydrogen atoms are at same height or to the nearer hydrogen atom if one of them is closer to the surface than the other. And the distances r_{H-H} are bond lengths between hydrogen atoms in calculations.

Fig. 1(c), (d), and (g) shows the adsorbed geometries of hydrogen molecule on MgO(0 0 1) surface at top sites. For the vertical approach, the distances r_d of H_2 from the MgO(0 0 1) surface are about 2.155 Å (O–H) and 2.355 Å (Mg–H), respectively. The H–H bond lengths are stretched up to 0.779 Å and 0.769 Å from the optimized bond length of 0.749 Å of the H_2 molecule; the adsorption energies are basically degenerate to 0.015 eV and −0.054 eV for on-top(O) and on-top(Mg), respectively. For the horizontal approach, the distance of the closer hydrogen atom to the MgO(0 0 1) surface is 2.195 Å with an adsorption energy of 0.052 eV at on-top(Mg) sites while the adsorption of H_2 at on-top(O) sites is unstable with respect to move to adjacent on-top(Mg) sites which has the second highest adsorption energy of hydrogen molecule on MgO surfaces. Obviously, for all the approaches, the H_2 adsorption is molecular and the maximum increase of the H–H bond length is only 0.030 Å for the vertical approach comparing with the optimized bond length of H_2. For the center sites, the vertical approach has adsorption energy of −0.015 eV. While for the calculation of horizontal approach, the molecular hydrogen moves to the bridge site with a vertical approach. This means that the center site is the most unstable site. For the bridge site, we find that the vertical approach has adsorption energy of 0.053 eV which is the highest among all other adsorption sites and approaches at the corresponding level of theories. In this site, the hydrogen molecule is relatively closer to the MgO surface with the distance of 2.078 Å. Compared with the energy in the vertical approach, the adsorption energy in the horizontal approach in the bridge site is less with a value of 0.042 eV.

From discussion above, it is clear that the initial adsorption of hydrogen on MgO(0 0 1) surface is primarily molecular in nature, and all the adsorption energies are very small and the same order. Also all the r_d are very large and, as a consequence, the r_H are similar to the optimized bond length of the hydrogen molecule. We should emphasize that the weakly bounded molecular state described above should be considered carefully as current implementations of DFT do not have the right physics to account for van der Waals interactions and consequently might not provide an accurate description of such weakly bound states [24].

In order to investigate the adsorption property of atomic H on an MgO(0 0 1) comprehensively, we calculated the potential energy surface (PES). A supercell configuration containing four monolayers was used for the PES calculations due to the computational expense. The calculation rules can be summarized as follows [25]. In the calculation, the substrate was relaxed to obtain more accurate results; hydrogen dynamics was restricted to the vertical direction after the H atom was introduced into the system. The analysis of the surface points to large energy differences between different places in the MgO cell. The energetically favorable place for the H atom is over the O^{2-} ion, the total energy being about −105.4 eV. It is interesting to note that the region of the lowest energy is near the oxygen site, the energy profile over the remaining part of the cell being rather flat. In the central region of the cell, the total energy increases up to about −105.0 eV. The shape of the energy surface rules out the possibility of an easy migration of the H atom over the MgO(0 0 1) surface. We cannot exclude, however, jumps to the neighboring oxygen sites either by the over-barrier mode (catalytic processes frequently proceed at rather high temperatures which makes activated jumps rather easy) or by the under-barrier (tunnelling) mode even at lower temperatures [24,26].

Table 3
Adsorbate height, bond length and adsorption energy for different adsorption sites considered for H atom adsorbed on MgO(0 0 1).

Site	r_l (Å)	r_d (Å)	Adsorption energy (eV)
On-top(O)	1.071 (O–H)	1.154	0.266029
On-top(Mg)	1.952 (Mg–H)	1.959	−0.424868
Center	2.098 (Mg–H) 2.140 (O–H)	1.529	−0.175853

The possible adsorption sites we examined for atomic hydrogen on clean MgO(0 0 1) are also shown in Fig. 1(a). The calculated adsorption energies for H atoms in different adsorption sites are presented in Table 3. Our results show that the differences of the adsorption energy for H atom at various sites are larger. H adsorption in a bridge site (Fig. 1) appeared to be unstable during optimization. And it can be seen that H atom at on-top(O) site has the highest adsorption energy among all other adsorption sites with the closer adsorbate height of 1.154 Å. For the on-top(Mg) site and center site, the binding energies increase to −0.42 and −0.18 eV, respectively. So, the most favorable site for H adsorption on MgO(0 0 1) surface is the on-top(O) position which is similar to our PES results.

3.3. Dissociation of H_2 molecule on MgO surface

Next, we present the dissociation pathways and the energy barriers for H_2 molecule adsorbing on MgO(0 0 1). One possible reaction pathway was investigated. In this set of calculations, we have considered the adsorption at two on-top(O) sites for initial state (IS) and final state (FS), starting from a configuration of H_2 molecule parallel to the surface. In the first step of calculation, the H_2 molecule was moved sequentially towards the surface and the atomic positions were allowed to relax in a plane parallel to the surface. Once the final adsorbed configurations have been determined, we performed the NEB calculation. The calculated dissociation pathway is plotted in Fig. 2. The IS, transition state, and FS are shown as insets in this figure. From discussion above, we know that the IS configuration is physisorption. Meanwhile, the H–H bond length is calculated to be 0.775 Å and the distance between the H atom and the nearest surface atom is 3.2 Å. In the transition state, the H–H bond length is 0.996 Å and the distance between the two different H atoms and the nearest surface O atom and Mg atom are 2.357 Å and 2.524 Å, respectively. After the transition state, one of H atoms breaks away and moves to the further on-top(O) site. Then the system descends through a flat step to reach the final state. The final state is at the on-top(O) site with a H–H bond length of 2.919 Å.

The dissociation energy barrier computed directly from the data in Fig. 2 is 2.2 eV without zero point energy corrections which is in agreement with the *ab initio* value (2.34–2.94 eV [9]). Comparing with clean Mg surface [27,28], yielding activation energies of 1.15 eV and 0.75 eV, it is shown that dissociation of H_2 on the MgO surface is more difficult. It means that, hydrogen adsorption in the close packed MgO is extremely slow [11] and the existence of a universal magnesium oxide passivation layers prevent H_2 molecule dissociating to atomic H.

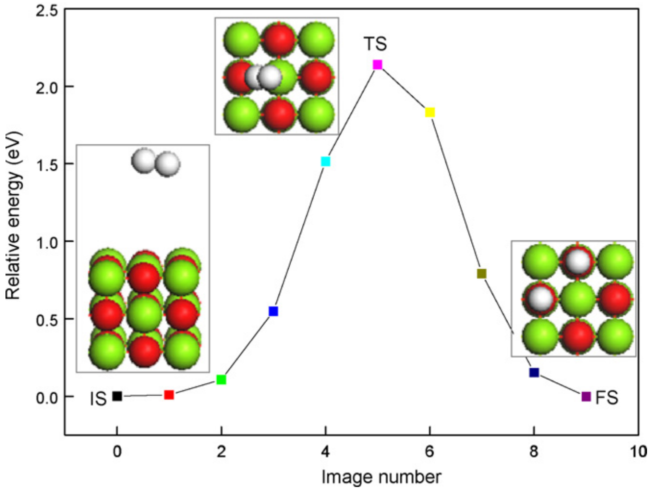

Fig. 2. The minimum energy pathway for a H_2 molecule dissociation on MgO(0 0 1). The NEB simulation consists of nine images. Zero-points energy corrects are not included.

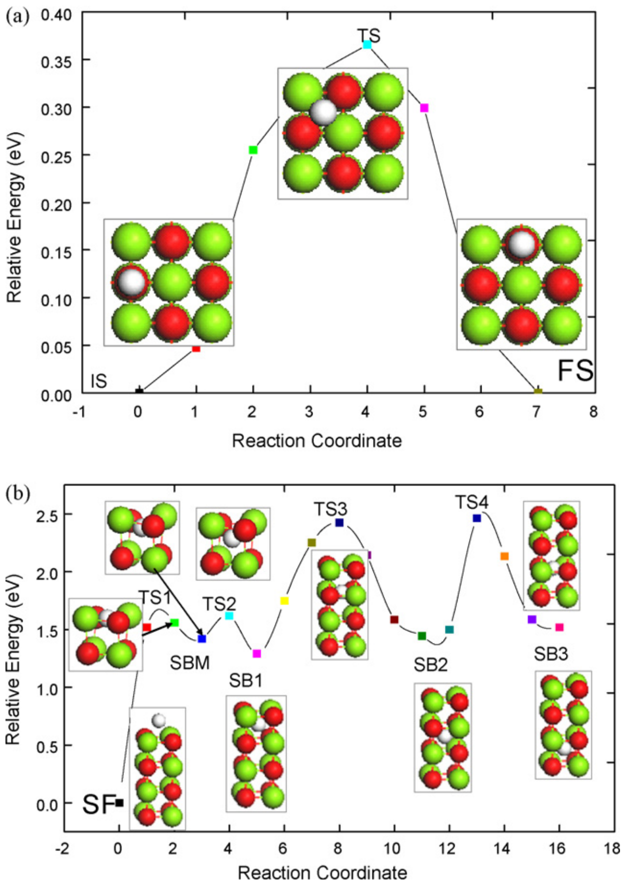

Fig. 3. The minimum-energy path for H diffusion on MgO(0 0 1) (a) and H diffusion from surface to subsurface (b). The NEB simulation consists of 7 and 16 images, respectively. Zero-points energy corrects are not included.

3.4. Diffusion of H atom on MgO surface and subsurface

We have shown in previous sections that the most stable configuration of atomic H on MgO(0 0 1) surface corresponds to adsorption at on-top(O) sites. Consequently, in order to characterize the surface diffusion we next considered the diffusion scenario of atomic hydrogen on the MgO(0 0 1) surface between two on-top(O) sites. And only one hydrogen atom is left in the unit cell. Because of only one stable configuration mentioned above, one pathway for atomic hydrogen diffusion was identified between two on-top(O) sites. The calculated minimum energy pathway is plotted in Fig. 3(a). Following the reaction coordinate, the classical barrier for surface diffusion is up to 0.37 eV. It should be noticed that the calculated diffusion barriers correspond only to a classical hopping model of diffusion. In practical cases, however, quantum tunneling effects should also be considered, particularly in the regime of low temperatures as mentioned above.

Then, we analyze the minimum energy pathway for atomic H diffusion from a surface adsorption site to subsurface sites. Firstly, we have determined a sequence of possible diffusion pathways involving octahedral adsorption sites SB1, SB2, and SB3 positioned at successively deeper layers and no other pathways are found here. Fig. 3(b) shows how H can diffuse into MgO(0 0 1) subsurfaces and the potential diagrams for the diffusion pathway is given. The classical diffusion barrier is about 1.52 eV from the initial SF to SB1 site. In this process, some special images, namely TS1, SBM and TS2 insetted in this figure, are found in our calculations. The (x, y) displacements for Mg atom in the first layer of three configurations are (+4.0%, +14.1%), (+7.7%, +9.9%) and (+6.4%, +17.3%) for TS2, TS1 and SBM, respectively. Meanwhile, the displacements for O atoms are $(-3.5\%, +2.8\%)$, $(-7.2\%, -1.6\%)$ and $(-1.6\%, -1.5\%)$, respectively. It can be seen that the Mg atoms give expansional scenario while O atoms present shrinkable properties due to the injected hydrogen. So, the lower total energy is accompanied by increasing of displacement for atoms. Once H atom reaches the second layer, activation energy of further diffusion towards the bulk is much lower. Our results show that the barrier from SB1 to SB2 step is about 1.2 eV while from SB2 to SB3 process it is 1.02 eV. Further diffusion barriers close to those obtained in bulk. When comparing these values to those obtained for surface diffusion, it is clear that diffusion of H atom towards the subsurface is less favorable. However, the barriers to subsurface sites can be overcome with temperature increase to make diffusion to subsurface sites possible [5].

The diffusion coefficient can be obtained according to the Arrhenius equation:

$$D = D_0\, e^{-E/RT} \tag{3}$$

It should be considered that the experiment results in Ref. [11] showed that the pre-exponential factor D_0 was about 150 $\mathrm{cm^2/s}$ under the temperature of 1173 K for D diffusion in the undoped MgO crystal. Therefore, the diffusion coefficient can be estimated using diffusion barriers of 0.37–1.52 eV in our model. The obtained value is about $3.85\text{–}0.44 \times 10^{-6}\ \mathrm{cm^2/s}$ which is general match with the experiments result of $(1.0 \pm 0.4) \times 10^{-6}\ \mathrm{cm^2/s}$.

Our results show that in this coverage the existence of oxygen will prevent the H_2 molecule dissociating to atomic H. This conclusion is in agreement with the common point of view: usually, oxide layers on the metal surface are not transparent to hydrogen molecules so that an MgO layer prevents hydrogen molecules from penetrating into the material. Recently, Ostenfeld et al. [28] found that by capping metallic magnesium films with oxide overlayers the apparent desorption energy of magnesium was increased from 1.5 eV to 3.2 eV. Interesting, there is also a special phenomena occurred in previous experiment results. Hjort et al. [29] found that the presence of Mg-oxide at the interface between magnesium and palladium could actually enhance the rate of hydrogen uptake, as compared with the clean surface of magnesium with a palladium overlayer. However, the hydrogenation improvement occurred only for a very thin layer of magnesium oxide. On the one hand it helps the nucleation of magnesium hydride, but on the other hand it reduces or even totally blocks hydrogenation when the oxide layer becomes thick and compact. Yoshimura et al. [30] have studied the same system, and found the fast hydrogenation of the magnesium film. Furthermore, the sputter profiles revealed that a vast amount of oxygen was present in the magnesium film, which could have influenced the hydriding kinetics. Considered displayed literatures above, it can be explained by the fact that thin oxides form a “patched” pattern on the surface and still allow hydrogen to diffuse into magnesium, whereas thicker oxides form a compact and non-permeable layer, which significantly reduces the hydrogenation rate. So, the magnesium oxide plays a dual role. Therefore, we speculate the correlative barriers should be difference with different oxygen coverages [31].

We believe that an increased understanding of the dynamics of hydrogen diffusion in magnesium oxide could possibly benefit for us to improve the kinetics of hydrogen sorption. Investigations by Gonzalez et al. [11], have studied the effect of various dopants on the diffusion of hydrogen in MgO. They found that the diffusion was markedly improved through the introduction of lithium into the system. Ultimately, it would seem that the diffusion behaviour of hydrogen in magnesium oxide phases is to be understood in greater detail, if magnesium-based systems are to be improved.

4. Conclusion

Using periodic density functional theory within the all-electron projector augmented wave formalism and the local density approximation to electron exchange and correlation, we have studied hydrogen adsorption on MgO surface. Our results show that H_2 molecule is weakly molecularly adsorbed on either the bridge or on-top(Mg) site of MgO(0 0 1). And on-top(O) position is the most favorable site with a binding energy value of 0.266 eV for atomic H adsorption on MgO(0 0 1) surface. The dissociation energy barrier computed is approximately 2.2 eV without zero point energy corrections. The minimum energy pathway for surface diffusion of atomic H indicates the existence of small classical barriers with value of about 0.37 eV. Finally, we calculate the atomic H diffuses from the surface sites to subsurface and further to the bulk sites. The largest barrier in these processes was obtained for the surface to subsurface step with a value of 1.52 eV and for diffusion among first and second layers underneath the surface with a barrier of 1.2 eV. Beyond second layer the diffusion barrier decreases to value close to 1.02 eV.

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